

# Excitations in a four-leg antiferromagnetic Heisenberg spin tube

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Inelastic neutron scattering is used to investigate magnetic excitations in the quasi-one-dimensional quantum spin-liquid system  $\text{Cu}_2\text{Cl}_4 \cdot \text{D}_8\text{C}_4\text{SO}_2$ . Contrary to previously conjectured models that relied on bond-alternating nearest neighbor interactions in the spin chains, the dominant interactions are actually next-nearest-neighbor in-chain antiferromagnetic couplings. The appropriate Heisenberg Hamiltonian is equivalent to that of a  $S = 1/2$  4-leg spin-tube with almost perfect one dimensionality and no bond alternation. A partial geometric frustration of rung interactions induces a small incommensurability of short-range spin correlations.

The  $S = 1/2$  antiferromagnetic (AF) Heisenberg spin ladder with an even number of legs is the cornerstone model in low-dimensional quantum magnetism [1, 2, 3, 4]. Its magnetic long range order is totally destroyed by zero-point quantum fluctuations, yet the “spin liquid” ground state is not entirely structureless, due to hidden topological non-local “string” correlations [5, 6]. Extensive theoretical studies lead to a profound understanding of spin ladders and related models, including the origin of the energy gap [1, 2, 3], multi-particle continua and bound states [4, 7], and the unique gapless quantum-critical phase that can be induced by external magnetic fields [8, 9]. Only a handful of experimental realizations of the ladder model have been found to date. Unfortunately, while some of these, like  $\text{IPa-CuCl}_3$  [10, 11], are not perfectly one-dimensional, others, like  $(\text{La,Ca,Sr})_{14}\text{Cu}_{24}\text{O}_{41}$  [12, 13], have energy scales and phase diagrams that can not be accessed in an experiment. The search for new prototype materials continues.

One compound recently discussed in this context is  $\text{Cu}_2\text{Cl}_4 \cdot \text{D}_8\text{C}_4\text{SO}_2$  (Sul- $\text{Cu}_2\text{Cl}_4$ ). It has a conveniently small spin gap  $\Delta \approx 0.5$  meV, and was described as being composed of  $S = 1/2$  double-chains with possible geometrically frustrated diagonal rung interactions [14, 15]. However, the gap in Sul- $\text{Cu}_2\text{Cl}_4$  could be fully accounted for without invoking the rung interactions, [14] by a slight structural alternation in the bond lengths. The corresponding bond-alternating  $S = 1/2$  chain can be viewed as an array of interacting AF spin dimers, like those found in  $\text{CuGeO}_3$  [16, 17] and  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{D}_2\text{O}$  [18]. Systems of this type realize a simple “local” spin liquid ground state that lacks the hidden symmetry violation or the translational invariance of the ladder model. Below we present the results of inelastic neutron scattering experiments that reveal that Sul- $\text{Cu}_2\text{Cl}_4$  is actually *not* a spin-dimer material, but neither it is a triangular ladder. Its key magnetic interactions lead to the formation of *uniformal 4-leg spin tubes* with no bond alternation and almost

perfect 1D character. A geometric frustration stabilizes unique *incommensurate* dynamic spin correlations.

Sul- $\text{Cu}_2\text{Cl}_4$  crystallizes in a triclinic space group  $P\bar{1}$  with  $a = 9.42$  Å,  $b = 10.79$  Å,  $c = 6.62$  Å,  $\alpha = 98.87^\circ$ ,  $\beta = 95.25^\circ$ , and  $\gamma = 120.85^\circ$  [14]. Pairs of  $S = 1/2$  chains built of edge-sharing  $\text{CuCl}_5\text{O}$  octahedra run along the crystallographic  $c$ -axis (Fig. 1). As mentioned above, due to the presence of two nonequivalent  $\text{Cu}^{2+}$  sites, there is a slight alternation (about 0.5%) in the distance between consecutive magnetic ions,  $\text{Cu}_1$  and  $\text{Cu}_2$ . In the original model of Ref. [14], these chains form the spin ladder legs, while the rungs involve nearby  $\text{Cu}^{2+}$  cations packed along the  $b$  axis. Both rung and leg magnetic interactions are established via  $\text{Cu-Cl-Cu}$  superexchange pathways. A key feature of this model is that the distance

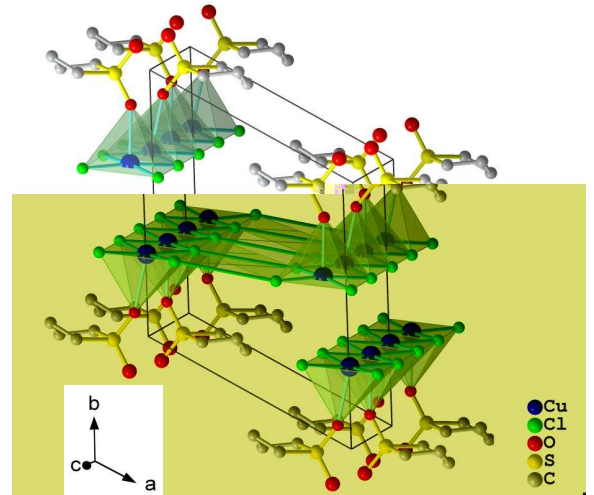


FIG. 1: (Color online) Schematic view of the crystal structure of Sul- $\text{Cu}_2\text{Cl}_4$ . Dominant AF interactions between  $S = 1/2$   $\text{Cu}^{2+}$  ions are mediated by  $\text{Cu-Cl-Cl-Cu}$  superexchange bridges.

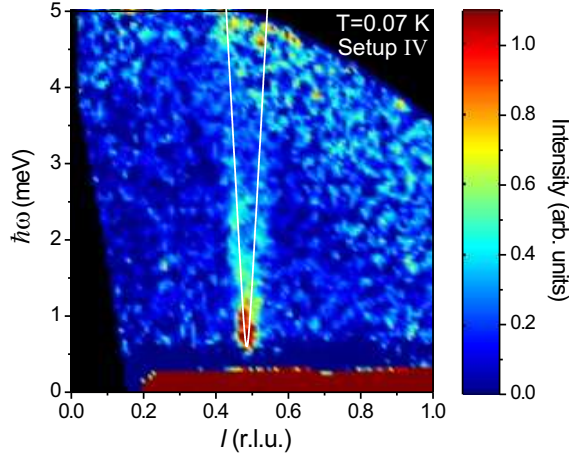


FIG. 2: Time of flight spectrum measured in Sul-Cu<sub>2</sub>Cl<sub>4</sub> in projection onto the  $c^*$  axis. The solid line is the fitted magnon dispersion relation, as described in the text.

between consecutive spins on each leg is  $c/2$ , so that the 1D AF zone-centers are located at integer values of  $l$ , where  $(h, k, l)$  are wave vector's reciprocal coordinates.

Previous neutron scattering studies employed thermal neutrons and protonated Sul-Cu<sub>2</sub>Cl<sub>4</sub> samples [19], but failed to detect any magnetic scattering. In our experiments we instead utilized fully deuterated Sul-Cu<sub>2</sub>Cl<sub>4</sub> single crystals, and put emphasis on cold neutron measurements. Most data were taken using ten to fifteen single crystals, with total masses of 1.5–2.5 g, co-aligned to an irregular cumulative mosaic of 3.5°. Inelastic data were collected on the SPINS cold-neutron 3-axis spectrometer at NCNR, with  $E_f = 3.7$  meV neutrons, a cooled BeO filter after the sample, and a horizontal focusing pyrolytic graphite (PG) analyzer (Setup I). Additional data were taken using the IN14 spectrometer at ILL, in a similar configuration (Setup II). Measurements with an enhanced wave vector resolution were performed on the V2 3-axis spectrometer at HMI, with a narrow focused PG analyzer and a smaller  $\sim 1$  g sample with a symmetric triangular mosaic spread of 1.9° (Setup III). Time-of-flight (TOF) experiments were performed at the Disc Chopper Spectrometer (DCS) at NCNR using a fixed incident energy  $E_i = 6.67$  meV (Setup IV).

A survey of the reciprocal space by a series of constant- $q$  and constant- $E$  scans revealed the inadequacy of the original model for Sul-Cu<sub>2</sub>Cl<sub>4</sub>. Figure 2 shows the energy- $l$  projection of the TOF spectrum measured at  $T = 70$  mK. It is immediately apparent that the 1D AF zone-center, where the spin gap  $\Delta$  is observed as a minimum in the magnetic excitation spectrum, is located near *half-integer* values of  $l$ . No low-energy magnetic scattering was detected at integer  $l$ . This behavior indicates that it is the next-nearest neighbor (NNN) spins in each chain which are strongly antiferromagnetically

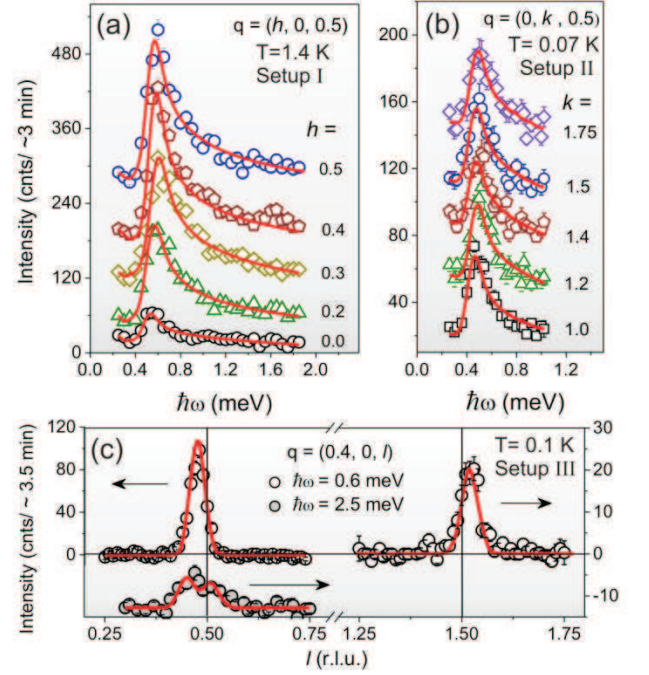


FIG. 3: (Color online) (a,b) Energy scans performed near the 1D AF zone center for different transverse wave vectors. (c) Constant-energy scans along the  $l$  direction measured just above the gap energy. Solid lines are fits to the data as described in the text.

correlated, not the nearest-neighbor ones as proposed in Refs. [14, 15]. The magnetic interactions responsible for strong NNN in-chain AF coupling are readily identified. They are established by superexchange across two-chlorine bridges, such as Cu<sub>1</sub>-Cl-Cl-Cu<sub>1</sub> or Cu<sub>2</sub>-Cl-Cl-Cu<sub>2</sub>. As was previously found in the structurally related material IPA-CuCl<sub>3</sub> [10], and in the Ni-based compound NiCl<sub>2</sub>-4SC(NH<sub>2</sub>)<sub>2</sub> [20], Cu-Cl-Cl-Cu couplings can be much stronger than those across single-halide Cu-Cl-Cu bridge due to more favorable bonding angles and orbital overlap. Thus, each alternating spin chain in Sul-Cu<sub>2</sub>Cl<sub>4</sub> should actually be considered as a pair of superimposed AF spin chains, each with a uniform (non-alternating) bond length equal to  $c$ . Such spin chains are highlighted by bold or dashed Cu-Cl-Cl-Cu bonds in Fig. 5a.

Our neutron data indicate that Sul-Cu<sub>2</sub>Cl<sub>4</sub> is indeed an exceptionally one-dimensional magnetic material. The dispersion of magnetic excitations is practically absent along the  $a^*$  and  $b^*$  axes (Fig. 3a,b), but very steep along the  $c^*$  direction (Fig. 2). Only the highest-resolution Setup III allowed us to estimate the corresponding spin wave velocity. Typical constant- $E$  scans are shown in Fig. 3c. At  $\hbar\omega = 0.6$  meV, just above the gap energy, resolution-limited peaks are observed. However, at 2.5 meV energy transfer, an intrinsic  $l$ -width becomes apparent and is due to a finite magnon velocity. As will be discussed below, the peaks are actually cen-

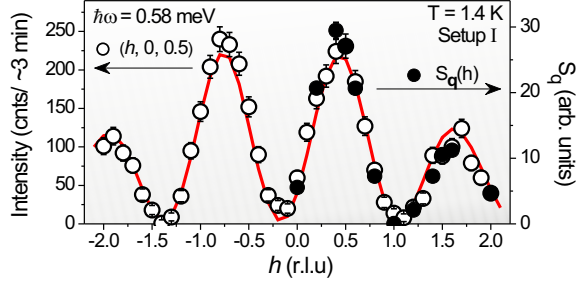


FIG. 4: Measured  $h$ -modulation of the scattering intensity of the energy-gap mode at  $T = 1.4$  K. Symbols and lines are as described in the text.

tered at *incommensurate* zone-centers  $l_0 = 0.5 - \delta$  and  $l_0 = 1.5 + \delta$ ,  $\delta = 0.022(2)$ . The approximate dispersion relation for low-energy magnons is therefore written as:

$$(\hbar\omega_{\mathbf{q}})^2 = \Delta^2 + v^2(\vec{q}\vec{c} - 2\pi l_0)^2. \quad (1)$$

A simple model cross section function can then be constructed using the single-mode approximation:

$$\frac{d^2\sigma}{d\Omega dE'} \propto |f(\mathbf{q})|^2 \frac{|F(\mathbf{q})|^2}{\hbar\omega_{\mathbf{q}}} \delta(\omega - \omega_{\mathbf{q}}), \quad (2)$$

where  $F(\mathbf{q})$  is the *a priori* unknown structure factor that is expected to be a smooth function of  $\mathbf{q}$ , and  $f(q)$  is the magnetic form factor for  $\text{Cu}^{2+}$ . Equation 2 convoluted with the known spectrometer resolution function was fit to the bulk of the 3-axis data to determine  $\Delta \simeq 0.55$  meV and  $v \simeq 14$  meV. Excellent fits are obtained and shown in solid lines in Fig. 3. The resulting dispersion curve is plotted over the TOF data in Fig. 2.

Having determined that Cu-Cl-Cl-Cu pathways dominate in-chain interactions, we now have to consider their role in the inter-chain coupling. As illustrated in Fig. 1, such bridges link pairs of adjacent  $\text{Cu}^{2+}$  chains in a plane *perpendicular* to the  $b$  axis. Note that these are *not* the same chain pairs as those considered in Ref. [14]. Recalling that each structural  $\text{Cu}^{2+}$  chain actually consists of two superimposed Heisenberg spin chains formed by NNN AF interactions, we find that Cu-Cl-Cl-Cu bridges in  $\text{Sul-Cu}_2\text{Cl}_4$  establish 4-leg spin “ladders”, as shown in Fig. 5a. In this representation  $J_1$  denotes the leg coupling responsible for a strong  $c$ -axis dispersion of magnetic excitations. In addition, three distinct “rung” interactions  $J_2$ ,  $J_3$  and  $J_4$  can be identified. None of these are affected by the bond alternation between the two distinct sites, Cu1 and Cu2. The four exchange pathways give  $\text{Sul-Cu}_2\text{Cl}_4$  the unique topology of a 4-leg spin tube, as shown in Fig. 5b.

The interactions  $J_2$ – $J_4$  establish correlations between the individual legs of each spin tube. Due to the resulting interference effect, the intensity of the gap mode becomes dependent on momentum transfer perpendicular to the

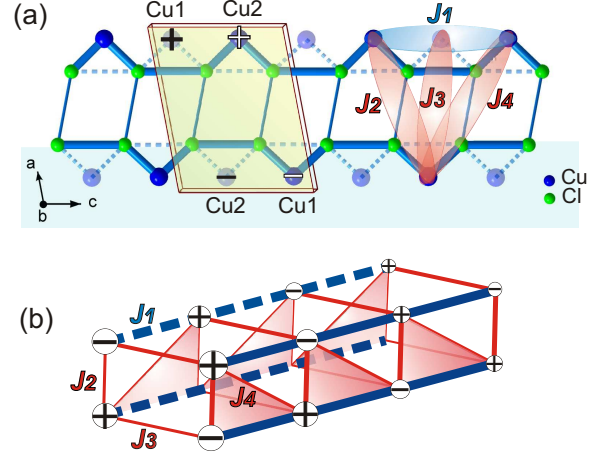


FIG. 5: (a) Ladder-like structure consisting of  $\text{Cu}^{2+}$  ions coupled through double chlorine bridges in  $\text{Sul-Cu}_2\text{Cl}_4$ . (b) A topologically equivalent uniform 4-leg spin tube structure. The relative instantaneous orientations of the spins are indicated by “+” and “-” signs.

chain axis. A constant- $E$  scan taken using Setup I just above the gap energy along the  $(h, 0, 0.5)$  direction, near the 1D zone-center, is shown in Fig. 4 (open circles) and reveals a strong intensity modulation. The solid symbols represent integrated intensities measured in  $l$ -scans of the type shown in Fig. 3c. The observed modulation is periodic, yet off-centered relative to  $h = 0$ . Similar behavior is seen at  $(h, 0, 1.5)$ . To explain this phenomenon quantitatively, we recall that in a simple 2-leg spin ladder the gap modes correspond to spins fluctuating coherently on the two ladder legs [2]. Their intensity is modulated by the modulus-squared of the rung’s structure factor. For AF rungs defined by a vector  $\mathbf{d}$ ,  $|F(\mathbf{q})|^2 = \sin^2(\mathbf{q}\mathbf{d}/2)$ . By analogy, the lowest-energy excitation of the 4-leg spin tube in  $\text{Sul-Cu}_2\text{Cl}_4$  is a coherent fluctuation of its four legs. The relative phases of the legs will depend on the details of the rung coupling. The intensity of the gap mode becomes modulated by the structure factor of the rung unit comprised of four spins, one on each leg:

$$F(\mathbf{q}) = \sum_{j=1}^4 \phi_j \exp(-i\mathbf{q}\mathbf{r}_j). \quad (3)$$

Here  $j$  labels the spins on the rung unit, and  $\phi_j = \pm 1$  are their corresponding phases. Since in our model inter-leg correlations are established by  $J_2$ ,  $J_3$  and  $J_4$ , only those spins directly connected by these interactions need be considered as members of a rung unit. Having tried all possible site and phase combinations, we found that only one can reproduce the measured transverse intensity modulation. The thus identified rung-unit is shown in Fig. 5a and coincides with the nominal crystallographic unit cell. The corresponding phases of its four spins are

indicated by “+” and “-” signs. This model, with ionic magnetic form factors and resolution effects taken into account, reproduces the observed intensity modulation almost perfectly, as shown in a solid line in Fig. 4. The 4-leg topology may also be responsible for the relatively small excitation gap in  $\text{Sul-Cu}_2\text{Cl}_4$  [22, 23].

Our model naturally accounts for the observed shift of the 1D AF zone-center relative to the commensurate position. We note that the diagonal AF interaction  $J_4$  incurs a geometric frustration relative to  $J_1-J_3$  (Fig. 5b). In classical magnets such frustration induces a helimagnetic state [24]. Theory predicts that in a frustrated quantum 2-leg spin ladder this incommensurability may survive in the equal-time spin correlation function [25], even though the ground state is disordered. In this case the minimum of the magnon dispersion occurs at an incommensurate wave vector. The situation in  $\text{Sul-Cu}_2\text{Cl}_4$  is a direct analogue of this effect in a spin tube with frustrating diagonals. Such a singlet ground state with incommensurate correlations has not been found in any previously studied 1D spin gap system.

We conclude that  $\text{Sul-Cu}_2\text{Cl}_4$  realizes the rare 4-leg spin tube model. The mapping is actually quite accurate: it is not at all perturbed by the intrinsic structural modulation of the  $\text{Cu}^{2+}$  chains, nor by three-dimensional interactions that are negligible. The spin tube Hamiltonian possesses unique quantum mechanical properties, due to periodic boundary conditions along the inter-chain direction. However, for previous lack of prototype materials, only a limited number of theoretical results have been accumulated [26, 27, 28]. Future work on  $\text{Sul-Cu}_2\text{Cl}_4$  should focus on higher-energy excitations, where one can expect to find exotic states with higher values of the transverse discrete quantum number. Magnetic field experiments will probe Bose-Einstein condensation of magnons. Due to geometric frustration, one can expect a unique helimagnetic high-field ordered phase.

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